|   | Туре | L #        | Hits   | Search Text         | DBs  | Time Stamp          |
|---|------|------------|--------|---------------------|--|---------------------|
| 1 | BRS  | L1         | 173626 | inert adj3 gas      | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:17 |
| 2 | BRS  | L2         | 725    | ruthenium near4 gas | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:19 |
| 3 | BRS  | L3         | 202698 | oxidation           | USPAT  | 2003/04/29<br>15:19 |
| 4 | BRS  | L4         | 401258 | oxidation           | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:19 |
| 5 | BRS  | <b>L</b> 5 | 1      | 1 same 2 same 4     | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:20 |
| 6 | BRS  | L6         | 133    |                     | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:20 |

|    | Туре | L#         | Hits   | Search Text  | DBs  | Time Stamp          |
|----|------|------------|--------|--|--|---------------------|
| 7  | BRS  | <b>L</b> 7 | 0      | 1 same 4 same 6  | USPAT; US-PGP UB; EPO; JPO; DERWEN T; IBM_TD B                         | 2003/04/29<br>15:20 |
| 8  | BRS  | L8         | 222663 | "O.sub.2" or "N.sub.20" or "H.sub.20" or "NO.sub.2" or "O.sub.3" | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:22 |
| 9  | BRS  | <b>L</b> 9 | 2      | 1 same 2 same 8  | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:32 |
| 10 | BRS  | L10        | 591935 | "N.sub.2" or He or Ar or Ne<br>or Xe                             | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:33 |
| 11 | BRS  | L11        | 24     | 2 same 8 same 10   | USPAT;<br>US-PGP<br>UB;<br>EPO;<br>JPO;<br>DERWEN<br>T;<br>IBM_TD<br>B | 2003/04/29<br>15:47 |

DOCUMENT-IDENTIFIER: US 20020058415 A1

TITLE: Methods for forming rough

ruthenium-containing layers

and structures/methods using same

----- KWIC -----

[0047] Preferably, the deposition rate for forming a rough ruthenium layer

14 while maintaining step coverage is a deposition rate in the range of about

100 .ANG./minute to about 500 .ANG./minute. More preferably, the deposition

rate is in a range of about 200 .ANG./minute to about 300 .ANG./minute. Yet

further, to maintain the step coverage with a high concentration of

ruthenium-containing precursor provided to the reaction chamber, preferably, a

flow rate of about 100 sccm to about 500 sccm of carrier gas (e.g., He,

O.sub.2, or any other gas that is non-reactive with the precursor) through a

ruthenium-containing precursor held in a bubbler reservoir at a temperature of

about 15.degree. C. to about 100.degree. C. is provided to the chamber. More

preferably, the flow rate of carrier gas through the ruthenium-containing

precursor to the reaction chamber is at a rate in the range of about 150 sccm to about 250 sccm.

DOCUMENT-IDENTIFIER: US 20020055254 A1

TITLE: Semiconductor device manufacturing

method and substrate

processing apparatus

----- KWIC -----

[0029] Next, reference will be made to the timing of supplying the gases,

which is characteristic of the semiconductor device manufacturing method

according to the present invention, while referring to FIG. 1. First, as

described above, the silicon wafer 30 disposed on the susceptor 29 in the

semiconductor manufacturing apparatus is lifted to the deposition position in

the reaction chamber 32, where the silicon wafer 30 is heated up to a

temperature of 290-350.degree. C. by means of the heater 27. Subsequently, an

N.sub.2 gas, which does not contribute to deposition
reactions, is supplied to

the reaction chamber in an amount of k sccm. Here, note that the amount of the

gas supply k sccm is an amount of supply by which the pressure in the reaction

chamber 32 can be held in a range of 60-180 Pa. Then, the amount of the

N.sub.2 gas supplied is adjusted to a range of 1,250-1,500 sccm, and the

pressure in the reaction chamber 32 is raised to a value ranging from 60 to

4,000 Pa. Thereafter, a raw material gas containing ruthenium such as, for

example, a gas evaporated from a liquid raw material Ru(C.sub.2H.sub.5C.sub.5H.sub.4).su- b.2(referred to as bisethyl-cyclopentadienyl-ruthenium), is supplied from the ruthenium raw gas

supply pipe 24a to the reaction chamber 32 in an amount of supply ranging from

0.005 to 0.12 sccm while decreasing the amount of supply of the N.sub.2 gas,

thereby holding the pressure in the reaction chamber 32 at a range of 60-4,000

Pa. Subsequently, after the amount of supply of the ruthenium raw gas has

become constant or steady, an oxygen-containing gas containing oxygen such as,

for instance, an <a>O.sub.2</a> gas, is supplied to the reaction chamber from the

oxygen-containing gas supply pipe 24b in an amount of supply ranging from 40 to

1,500 sccm while decreasing the amount of supply of the N.sub.2 gas to a value

ranging from 0 to 710 sccm, thereby holding the pressure in the reaction

chamber 32 in a range of 60-4,000 Pa. Here, note that an O.sub.3 gas or an

N.sub.20 gas may be used as the oxygen-containing gas. In this manner, the

deposition of ruthenium films is initiated. That is, the ruthenium raw gas is

supplied prior to or earlier than the oxygen-containing gas, so that the oxygen

ratio, i.e., the volume ratio of the oxygen-containing gas
to the ruthenium raw

gas, before the start of deposition of the ruthenium films
is controlled to be

smaller than the oxygen ratio at the time of deposition, and not greater than a

value at which there takes place no deposition reaction in
which ruthenium is

separated from the ruthenium raw gas. Then, the amount of the

oxygen-containing gas to be supplied is decreased, and thereafter the amount of

the <u>ruthenium raw gas</u> to be supplied is also decreased. Thus, after the supply

of the oxygen-containing gas is stopped, the supply of the ruthenium raw gas is

also stopped, and the amount of the N.sub.2 gas to be supplied is increased to

a value ranging from 1,250 to 1,500 sccm, thereby holding the pressure in the

reaction chamber 32 at a value ranging from 60 to 4,000 Pa. In this manner,

the deposition of the ruthenium films is completed. After this, the amount of

the N.sub.2 gas to be supplied is decreased to a value of k

sccm, whereby the pressure in the reaction chamber 32 is held at a level in the range of 60-180 Pa.

US-PAT-NO:

6461961

DOCUMENT-IDENTIFIER:

US 6461961 B1

TITLE:

Methods of manufacturing

semiconductor devices with

ruthenium films formed by CVD using

an oxygen-containing

reactant gas

### ----- KWIC -----

Next, reference will be made to the timing of supplying the gases, which is

characteristic of the semiconductor device manufacturing method according to

the present invention, while referring to FIG. 1. First, as described above,

the silicon wafer 30 disposed on the susceptor 29 in the  $\operatorname{semiconductor}$ 

manufacturing apparatus is lifted to the deposition position in the reaction

chamber 32, where the silicon wafer 30 is heated up to a temperature of  $\frac{1}{2}$ 

290-350.degree. C. by means of the heater 27.

Subsequently, an N.sub.2 gas,

which does not contribute to deposition reactions, is supplied to the reaction

chamber in an amount of k sccm. Here, note that the amount of the gas supply k

sccm is an amount of supply by which the pressure in the reaction chamber 32

can be held in a range of 60-180 Pa. Then, the amount of the  ${\underline{\text{N.sub.2}}}$  gas

supplied is adjusted to a range of 1,250-1,500 sccm, and the pressure in the

reaction chamber 32 is raised to a value ranging from 60 to 4,000 Pa.

Thereafter, a raw material gas containing ruthenium such as, for example, a gas

evaporated from a liquid raw material Ru(C.sub.2 H.sub.5 C.sub.5 H.sub.4).sub.2

(referred to as bisethyl-cyclopentadienyl-ruthenium), is supplied from the

ruthenium raw gas supply pipe 24a to the reaction chamber
32 in an amount of

supply ranging from 0.005 to 0.12 sccm while decreasing the amount of supply of

the  $\underline{\text{N.sub.2}}$  gas, thereby holding the pressure in the reaction chamber 32 at a

range of 60-4,000 Pa. Subsequently, after the amount of supply of the

ruthenium raw gas has become constant or steady, an oxygen-containing gas

containing oxygen such as, for instance, an  $\underline{\text{O.sub.2}}$  gas, is supplied to the

reaction chamber from the oxygen-containing gas supply pipe 24b in an amount of

supply ranging from 40 to 1,500 sccm while decreasing the amount of supply of  $\,$ 

the  $\underline{\text{N.sub.2}}$  gas to a value ranging from 0 to 710 sccm, thereby holding the

pressure in the reaction chamber 32 in a range of 60-4,000 Pa. Here, note that

an  $\underline{\text{O.sub.3}}$  gas or an  $\underline{\text{N.sub.2}}$  O gas may be used as the oxygen-containing gas.

In this manner, the deposition of ruthenium films is initiated. That is, the

ruthenium raw gas is supplied prior to or earlier than the
oxygen-containing

gas, so that the oxygen ratio, i.e., the volume ratio of the oxygen-containing

# gas to the ruthenium raw gas, before the start of deposition of the ruthenium

films is controlled to be smaller than the oxygen ratio at the time of

deposition, and not greater than a value at which there takes place no

deposition reaction in which <u>ruthenium is separated from</u> the ruthenium raw gas.

Then, the amount of the oxygen-containing gas to be supplied is decreased, and

thereafter the amount of the  $\underline{\textbf{ruthenium raw gas}}$  to be supplied is also

decreased. Thus, after the supply of the oxygen-containing gas is stopped, the

supply of the ruthenium raw gas is also stopped, and the
amount of the N.sub.2

gas to be supplied is increased to a value ranging from 1,250 to 1,500 sccm,

thereby holding the pressure in the reaction chamber 32 at

a value ranging from 60 to 4,000 Pa. In this manner, the deposition of the ruthenium films is completed. After this, the amount of the N.sub.2 gas to be supplied is decreased to a value of k sccm, whereby the pressure in the reaction chamber 32 is held at a level in the range of 60-180 Pa.

US-PAT-NO:

6429127

DOCUMENT-IDENTIFIER:

US 6429127 B1

TITLE:

Methods for forming rough

ruthenium-containing layers

and structures/methods using same

----- KWIC -----

Preferably, the deposition rate for forming a rough ruthenium layer 14 while maintaining step coverage is a deposition rate in the range

of about 100

.ANG./minute to about 500 .ANG./minute. More preferably, the deposition rate  $\,$ 

is in a range of about 200 .ANG./minute to about 300 .ANG./minute. Yet

further, to maintain the step coverage with a high concentration of

ruthenium-containing precursor provided to the reaction chamber, preferably, a

flow rate of about 100 sccm to about 500 sccm of carrier gas (e.g., He,

O.sub.2, or any other gas that is non-reactive with the precursor) through a

ruthenium-containing precursor held in a bubbler reservoir at a temperature of

about 15.degree. C. to about 100.degree. C. is provided to the chamber. More

preferably, the flow rate of carrier gas through the ruthenium-containing

precursor to the reaction chamber is at a rate in the range of about 150 sccm to about 250 sccm.

US-PAT-NO: 6335551

DOCUMENT-IDENTIFIER: US 6335551 B1

TITLE: Thin film capacitor having an

improved bottom electrode

and method of forming the same

### ----- KWIC -----

A first embodiment according to the present invention will be described in

detail with reference to FIG. 4 which is a fragmentary cross sectional

elevation view illustrative of a first novel thin film capacitor having an

improved bottom electrode formed over a semiconductor
substrate for a

semiconductor integrated circuit. A SiO.sub.2 passivation film 2 is provided

on a GaAs substrate 1. A Ti layer 3 having a thickness of 10 nanometers is

deposited as a contact layer on a selected region of the SiO.sub.2 passivation

film 2 by a sputtering method at room temperature. The GaAs substrate 1 is

cooled at a temperature of -100.degree. C. indirectly with a liquid nitrogen

before an amorphous ruthenium oxide thin film having a thickness of 100

nanometers is deposited on the Ti contact layer 3 by a reactive sputtering

method using an Ar-75% O.sub.2 mixture gas to form an amorphous ruthenium oxide

bottom electrode 4-1 on the Ti contact layer 3. An SrTiO.sub.3 thin dielectric

film 7 having a thickness of 200 nanometers is deposited on a selected region

of the amorphous ruthenium oxide bottom electrode 4-1 by an RF-sputtering

method at a temperature of 200.degree. C. A Pt top electrode 8 is provided on

the SrTiO.sub.3 thin dielectric film 7. A SiO.sub.2 interlayer insulator 5 is

entirely provided which extends over the Pt top electrode 8, the SrTiO.sub.3 thin dielectric film 7, the amorphous ruthenium oxide bottom electrode 4-1 and the SiO.sub.2 passivation film 2. The SiO.sub.2 interlayer insulator 5 has contact holes positioned over the Pt top electrode 8 and the amorphous ruthenium oxide bottom electrode 4-1. A first Au interconnection layer 6-1 is provided over the SiO.sub.2 interlayer insulator 5 and within the contact hole positioned over the amorphous ruthenium oxide bottom electrode 4-1, so that the first Au interconnection layer 6 is in contact with the amorphous ruthenium oxide bottom electrode 4-1. A second Au interconnection layer 6-2 is provided over the SiO.sub.2 interlayer insulator 5 and within the contact hole positioned over the Pt top electrode 8, so that the second Au interconnection layer 6 is in contact with the Pt top electrode 8.

A fourth embodiment according to the present invention will be described in detail with reference to FIG. 8 which is a fragmentary cross sectional elevation view illustrative of a fourth novel thin film capacitor having an improved bottom electrode formed over a semiconductor substrate for a semiconductor integrated circuit. A TiSi.sub.2 first diffusion barrier layer 10 is provided on a Si substrate 9. A TiN second diffusion barrier layer 11 is provided on the TiSi.sub.2 first diffusion barrier layer An Ir third diffusion barrier layer 12a is provided on the TiN second diffusion barrier layer 11. The Si substrate 9 is cooled at a temperature of -100.degree. C. indirectly with a liquid nitrogen before an amorphous ruthenium oxide thin film is deposited on the Ir third diffusion barrier layer 12a by a reactive sputtering method using an Ar-75% O.sub.2 mixture gas to form an amorphous

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ruthenium oxide bottom electrode 13a on the Ir third
diffusion barrier layer
12a. A (Ba.sub.0.5 Sr.sub.0.5) TiO.sub.3 first thin
dielectric film 14 having a
thickness of 10 nanometers is deposited on the amorphous
ruthenium oxide bottom
electrode 13a by an RF-sputtering method at a temperature
of 300.degree. C.,
whereby a smooth interface with a small roughness is formed
between the
amorphous ruthenium oxide bottom electrode 13a and the
(Ba.sub.0.5
Sr.sub.O.5) TiO3 first thin dielectric film 14. A
(Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 second thin dielectric film 15 having
a thickness of 200
nanometers is deposited on the (Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 first thin
dielectric film 14 by an RF-sputtering method at a higher
temperature of
450.degree. C., whereby the above amorphous ruthenium
oxide bottom electrode
13a is crystallized to form a single crystal ruthenium
oxide bottom electrode
13a. Since, however, the smooth interface has already been
defined between the
amorphous ruthenium oxide bottom electrode 13a and the
(Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 first thin dielectric film 14, the
interface between the
single crystal ruthenium oxide bottom electrode 13a and the
(Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 first thin dielectric film 14 remains
smooth. Namely, the
high flatness of the surface of the single crystal
ruthenium oxide bottom
electrode 13a can be obtained. Since, further, the
(Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 second thin dielectric film 15 is
formed by the higher
temperature than when the (Ba.sub.0.5 Sr.sub.0.5) TiO.sub.3
first thin
dielectric film 14 is formed, then the (Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 second
thin dielectric film 15 has a higher dielectric constant
than the (Ba.sub.0.5
Sr.sub.0.5) TiO.sub.3 first thin dielectric film 14. Since,
furthermore, the
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(Ba.sub.0.5 Sr.sub.0.5) TiO.sub.3 second thin dielectric film 15 is much thicker than the (Ba.sub.0.5 Sr.sub.0.5) TiO.sub.3 first thin dielectric film 14, a dielectric constant of the capacitor largely depends upon the higher dielectric constant of the (Ba.sub.0.5 Sr.sub.0.5) TiO.sub.3 second thin dielectric film Thus, the above structure makes it possible to obtain 15. both the required smooth interface between the bottom electrode and the dielectric film of the capacitor and the required high dielectric constant of the capacitor. An Ru top electrode 16 is provided on the (Ba.sub.0.5 Sr.sub.0.5) TiO.sub.3 second thin dielectric film 15.

A fifth embodiment according to the present invention will be described in detail with reference to FIG. 10 which is a fragmentary cross sectional elevation view illustrative of a fifth novel thin film capacitor having an improved bottom electrode formed over a semiconductor substrate for a semiconductor integrated circuit. A TiSi.sub.2 first diffusion barrier layer 10 is provided on a Si substrate 9. A TiN second diffusion barrier layer 11 is provided on the TiSi.sub.2 first diffusion barrier layer An Ru third diffusion barrier layer 12a is provided on the TiN second diffusion barrier layer 11. The Si substrate 9 is cooled at a temperature of -100.degree. C. indirectly with a liquid nitrogen before an amorphous ruthenium oxide thin film is deposited on the Ru third diffusion barrier layer 12 by a reactive sputtering method using an Ar-75% O.sub.2 mixture gas to form an amorphous strontium ruthenium oxide SrRuO.sub.3 layer on the Ru third diffusion barrier layer 12. A Pb(Zr.sub.0.48 Ti.sub.0.52)O.sub.3 thin film

layer 12. A Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin fill having a thickness of 200 nanometers is deposited on the amorphous strontium ruthenium oxide

SrRuO.sub.3 layer by an RF-sputtering method at a temperature of 300.degree. C., before the whereby a smooth interface with a small roughness is formed between the Pb(Zr.sub.0.48 Ti.sub.0.52)O.sub.3 thin film is subjected to a rapid thermal annealing in an oxygen atmosphere at a temperature of 600.degree. C. for 30 seconds to cause a crystallization of the amorphous strontium ruthenium oxide SrRuO.sub.3 layer thereby to form a strontium ruthenium oxide SrRuO.sub.3 bottom electrode 17-1 and also to form a Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin dielectric film 18 on the strontium ruthenium oxide SrRuO.sub.3 bottom electrode 17-1. An Ru top electrode 16 is provided on the Pb(Zr.sub.0.48 Ti.sub.0.52)O.sub.3 thin dielectric film 18. During the deposition process of the Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin film at the temperature of 300.degree. C., no crystallization is caused to the amorphous strontium ruthenium oxide SrRuO.sub.3 layer, for which reason the smooth surface of the amorphous strontium ruthenium oxide SrRuO.sub.3 layer remains unchanged, whereby the smooth interface can be obtained between the amorphous strontium ruthenium oxide SrRuO.sub.3 bottom electrode 17-1 and the amorphous Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin film. During the subsequent rapid thermal annealing at the temperature of 600.degree. C. for forming the Pb(Zr.sub.0.48 Ti.sub.0.52)O.sub.3 thin dielectric film 18, the amorphous strontium ruthenium oxide SrRuO.sub.3 layer is crystallized to form the strontium ruthenium oxide SrRuO.sub.3 bottom electrode Notwithstanding, the smooth interface between the amorphous strontium ruthenium oxide SrRuO.sub.3 layer and the Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin film has already been defined, for which reason the smooth interface can be obtained

between the strontium ruthenium oxide SrRuO.sub.3 bottom electrode 17-1 and the

Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin dielectric film 18. Further, the

Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin dielectric film 18 is formed by the

high temperature annealing, for which reason the Pb(Zr.sub.0.48

Ti.sub.0.52) O.sub.3 thin dielectric film 18 has a high dielectric constant.

Thus, the above structure makes it possible to obtain both the required smooth

interface between the bottom electrode and the dielectric film of the capacitor

and the required high dielectric constant of the capacitor.

A sixth embodiment according to the present invention will be described in

detail with reference to FIG. 11 which is a fragmentary cross sectional

elevation view illustrative of a sixth novel thin film capacitor having an

improved bottom electrode formed over a semiconductor substrate for a

semiconductor integrated circuit. A TiSi.sub.2 first diffusion barrier layer

10 is provided on a Si substrate 9. A TiN second diffusion barrier layer 11 is

provided on the TiSi.sub.2 first diffusion barrier layer 10. An Ru third

diffusion barrier layer 12a is provided on the TiN second diffusion barrier

layer 11. The Si substrate 9 is cooled at a temperature of -100.degree. C.

indirectly with a liquid nitrogen before an amorphous ruthenium oxide thin film

is deposited on the Ru third diffusion barrier layer 12 by a reactive

sputtering method using an Ar-75% O.sub.2 mixture gas to form an amorphous

strontium ruthenium oxide SrRuO.sub.3 layer including 5 at
% of Mg on the Ru

third diffusion barrier layer 12. A Pb(Zr.sub.0.48 Ti.sub.0.52)O.sub.3 thin

film having a thickness of 200 nanometers is deposited on the 5 at %

Mg-containing amorphous strontium ruthenium oxide SrRuO.sub.3 layer by an

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RF-sputtering method at a temperature of 300.degree. C.,
before the whereby a
smooth interface with a small roughness is formed between
the Pb(Zr.sub.0.48
Ti.sub.0.52) O.sub.3 thin film is subjected to a rapid
thermal annealing in an
oxygen atmosphere at a temperature of 600.degree. C. for
30 seconds to cause a
crystallization of the 5 at % Mg-containing amorphous
strontium ruthenium oxide
SrRuO.sub.3 layer thereby to form a 5 at % Mg-containing
strontium ruthenium
oxide SrRuO.sub.3 bottom electrode 17-2 and also to form a
Pb(Zr.sub.0.48
Ti.sub.0.52) O.sub.3 thin dielectric film 18 on the 5 at %
Mg-containing
strontium ruthenium oxide SrRuO.sub.3 bottom electrode
17-2. An Ru top
electrode 16 is provided on the Pb(Zr.sub.0.48
Ti.sub.0.52) O.sub.3 thin
dielectric film 18. During the deposition process of the
Pb(Zr.sub.0.48
Ti.sub.0.52) O.sub.3 thin film at the temperature of
300.degree. C., no
crystallization is caused to the 5 at % Mg-containing
amorphous strontium
ruthenium oxide SrRuO.sub.3 layer, for which reason the
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smooth surface of the 5
at % Mg-containing amorphous strontium ruthenium oxide

SrRuO.sub.3 layer remains unchanged, whereby the smooth interface can be

obtained between the 5 at % Mg-containing amorphous strontium ruthenium oxide

SrRuO.sub.3 bottom

electrode 17-2 and the amorphous Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin film.

During the subsequent rapid thermal annealing at the temperature of 600.degree.

C. for forming the Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin dielectric film 18,

the 5 at % Mg-containing amorphous strontium ruthenium oxide SrRuO.sub.3 layer

is crystallized to form the 5 at % Mg-containing strontium ruthenium oxide

SrRuO.sub.3 bottom electrode 17-2. Notwithstanding, the smooth interface

between the 5 at % Mg-containing amorphous strontium ruthenium oxide

SrRuO.sub.3 layer and the Pb(Zr.sub.0.48

Ti.sub.0.52) O.sub.3 thin film has

already been defined, for which reason the smooth interface can be obtained

between the 5 at % Mg-containing strontium ruthenium oxide SrRuO.sub.3 bottom

electrode 17-2 and the Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin dielectric film

18. Further, the Pb(Zr.sub.0.48 Ti.sub.0.52) O.sub.3 thin dielectric film 18 is

formed by the high temperature annealing, for which reason the Pb(Zr.sub.0.48

Ti.sub.0.52) O.sub.3 thin dielectric film 18 has a high dielectric constant.

Thus, the above structure makes it possible to obtain both the required smooth

interface between the bottom electrode and the dielectric film of the capacitor

and the required high dielectric constant of the capacitor.

US-PAT-NO: 6287934

DOCUMENT-IDENTIFIER: US 6287934 B1

TITLE:

Capacitor structure of semiconductor

memory cell and

method for fabricating capacitor

structure of

semiconductor cell

----- KWIC -----

Subsequently, DC sputtering is performed using Ru (ruthenium) as the and

O.sub.2 /Ar as the process gas to form the lower electrode layer 21A made of

RuO.sub.2 on the entire surface involving the insulation material layer 40.

The lower electrode layer 21A is then dry-etched by RIE using O.sub.2

/Cl.sub.2. In this manner, the semi-spherical insulation material layer 40

made of SiN, and the lower electrode made of the lower electrode layer 21A

stacked on the insulation material layer 40, can be obtained. Note here that

dry-etching of the lower electrode layer 21A is conducted for patterning the

lower electrode layer 21A, and not for shaping the lower electrode layer 21

semi-spherical. The surface of the lower electrode layer 21A on which the

ferroelectric thin film should be made is covered by the resist material during

etching of the lower electrode layer 21A. Therefore, the ferroelectric thin

film can be formed on the lower electrode layer 21A maintaining its original

surface condition, and deterioration in P-E hysteresis loop characteristics of

the ferroelectric thin film can be prevented.

DOCUMENT-IDENTIFIER: US 20020190276 A1

TITLE: Process for the formation of

RuSixOy-containing barrier

layers for high-k dielectrics

#### ----- KWIC -----

[0076] More specifically, deposition of monolayers is accomplished in a CVD

chamber, as previously described with reference to the CVD deposition method,

but with the addition of pulsing valves to allow the switching between the

precursor and purge gas and the SiH.sub.4 (Si.sub.2H.sub.6) and purge gas.

Bubblers, however, are not required since carrier gases may or may not be used,

depending on the configuration of the vacuum system. For this example, a

simple storage ampule with a single outlet and no inlet is used. As with the

CVD method, C.sub.6H.sub.8Ru(CO).sub.3 is used as the ruthenium precursor. The

deposition temperature of the wafer surface is 50-250 degrees C. and the

reaction chamber is kept at a variable pressure range of about 0.5 torr to

about 0.0001 torr. The reaction chamber is fully opened to the pumps of the

vacuum system to create a vacuum in the CVD chamber and the ruthenium precursor

gas is introduced at low pressure, preferably about 0.0001
torr. Introduction

of the <u>ruthenium precursor gas</u> under these conditions will result in the

deposition of, at most, a monolayer of ruthenium over the surface of the wafer.

A purge cycle is then initiated by introducing a nonreactive gas, such as **He or** 

Ar, at a volumetric flow rate of about 50 sccm into the reaction chamber at 0.5

torr. It is understood that any suitable nonreactive gas may be used and that

DOCUMENT-IDENTIFIER: US 20010039115 A1

TITLE: Method and apparatus for

manufacturing semiconductor

devices

----- KWIC -----

[0035] In addition, the ratio of the flow rate of the ruthenium raw gas to

the flow rate of the gas containing oxygen atoms (i.e., oxygen (O.sub.2), ozone

(O.sub.3), etc.) is not particularly limited but can be properly determined

according to the kind of the films (i.e., ruthenium films or ruthenium oxide

films) formed on a substrate. Also, the carrier gas, being caused to flow

through the carrier gas pipe 11 for transportation of the ruthenium raw gas,

can be properly selected from known ones, and for instance, an inert gas such

as a nitrogen (N.sub.2) gas, an argon (Ar) gas or the like may be used for such a purpose.

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TITLE: Process for the formation of

RuSixOy-containing barrier

layers for high-k dielectrics

## ----- KWIC -----

[0078] More specifically, deposition of monolayers is accomplished in a  $\ensuremath{\mathsf{CVD}}$ 

chamber, as previously described with reference to the CVD deposition method,

but with the addition of pulsing valves to allow the switching between the

precursor and purge gas and the SiH.sub.4 (Si.sub.2H.sub.6) and purge gas.

Bubblers, however, are not required since carrier gases may or may not be used,

depending on the configuration of the vacuum system. For this example, a

simple storage ampule with a single outlet and no inlet is used. As with the

CVD method, C.sub.6H.sub.8Ru(CO).sub.3 is used as the ruthenium precursor. The

deposition temperature of the wafer surface is 50-250 degrees C. and the

reaction chamber is kept at a variable pressure range of about 0.5 torr to

about 0.0001 torr. The reaction chamber is fully opened to the pumps of the  $\ensuremath{\text{c}}$ 

vacuum system to create a vacuum in the CVD chamber and the ruthenium precursor

gas is introduced at low pressure, preferably about 0.0001 torr. Introduction

of the ruthenium precursor gas under these conditions will result in the

deposition of, at most, a monolayer of ruthenium over the surface of the wafer.

A purge cycle is then initiated by introducing a nonreactive gas, such as **He or** 

Ar, at a volumetric flow rate of about 50 sccm into the reaction chamber at 0.5

torr. It is understood that any suitable nonreactive gas may be used and that

the nonreactive gas may be introduced at a rate of between about 0.1 sccm to about 500 sccm to optimize system conditions. Silane or disilane is introduced into the reaction chamber at a rate of about 5 sccm, which results in the deposition of a silicon monolayer over the previously deposited ruthenium monolayer. This is followed by a purge cycle of nonreactive gas, as previously described. It is understood that oxygen can be added as a separate oxygen/purge cycle as needed for every individual cycle in order to give the required oxygen content. In general, however, sufficient oxygen is available from background O.sub.2 and H.sub.20 in the chamber to

oxidize the underlying
RuSi.sub.x layer formed in the preceding steps. The
monolayer of adsorbed

precursor from the initial precursor deposition step will react directly when

exposed to the reaction gas in the third step of the foregoing dose

precursor/purge/dose reaction gas/purge sequence, which results in controlled

deposition of one or more RuSi.sub.xO.sub.y-containing barrier monolayers.